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Effect of mechanical recycling on the properties of a composite material based on polyvinyl chloride loaded with olive husk flour

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Abstract

In this article, we try to contribute to the development of methods and strategies necessary to transform olive husk (OH) from waste for disposal into valuable raw materials as bio-filler for the PVC, for providing a composite with very high physical-mechanical and thermal characteristics interesting.Several formulations of composite materials based on PVC (as a matrix), olive husk (as filler) and a PVC-g-MA coupling agent, have been the subject of study experiments to assess the structural-mechanical and thermal properties. Investigate the combined effect of olive husk flour, PVC-g-MA and recycling on composite properties.

The results showed that the mechanical properties of the composites increase with the number of extrusion cycles, the tensile strength and the Young's modulus in the studied formulations increased considerably. On the other hand, the infrared spectra show no significant change after four extrusion cycles. It is also important to take into account the evolution of the thermal properties of the composites after the transformation cycles. We noticed that the addition of olive husk flour causes a slight decrease in the temperature of onset of degradation.

Keywords:*Lignocellulosic flour, Polyvinyl chloride, recycling, mechanical properties, thermal behavior.*

I. Introduction

Nowadays, the need to preserve the environment and save energy has become more than necessary for the future of the planet. In the face of this, environmental degradation and climate change affect humanity. The development of plant resources produced by the Algerian soil provides a very interesting alternative to environmental problems and the probable depletion of fossil resources. Olive pomace, one of these natural resources, is a by-product of waste from various oil mills. Every year, thousands of tons of this product are incinerated or simply released into nature, causing major inconvenience for the environment [1,2]. It is the abundance of this waste that motivated the choice of olive husk flour as feedstock in the manufacture of composite materials.

Natural fiber composite materials occupy an important place in the history of technology. The increasing use of vegetable fibers as reinforcements in composites with thermosetting or thermoplastic matrices provides very interesting environmental advantages. However, the strongly hydrophilic nature of the fiber weakens the interfacial bond with the hydrophobic matrices but this problem of incompatibility has been resolved by the development of original techniques for improving adhesion, the various techniques tried can be divided into two categories: physical modification methods and chemical methods [3-5].

Composites are increasingly used in many industrial fields such as aeronautics, automotive, shipbuilding, infrastructure, etc. Indeed, they have many advantages compared to conventional materials reside in their performance, lightness and in particular good mechanical properties combined with low density, ease of handling during implementation and low production cost. Environmental concerns, both in terms of limiting the use of fossil resources and the need to manage the waste produced, have led to increased pressure to recycle materials [6,7]. The options available for waste disposal and management are recycling and/or reuse in different useful products.

Nadali et al [8]. were emphasized on closed-loop recycling of wood flour/poly (vinyl chloride) composites, since there is normally a considerable amount of material waste in wood plastic production lines. Composite materials were produced and subjected to four times reprocessing cycles under industrial conditions. Detailed analytical methods including bending strength, modulus of elasticity, impact strength, scanning electron microscopy, fiber length, water absorption, contact angle, Fourier transform infrared, and dynamic mechanical thermal analysis (DMTA) were conducted to evaluate the effects of recycling on the mentioned composites. Results demonstrated that the recycled composites, except for the four-time recycled ones, had lower bending strength, modulus of elasticity, and impact strength due to fiber-chain scission/fracture resulting from shear stress during reprocessing; however, impact strength remained almost unchanged after the first recycling cycle. Results also revealed that generally the reprocessed composites showed lower water absorption rates due to better fiber wetting and encapsulation. There was also a reduction in hemicellulose hydroxyl groups, rendering the recycled composites less hydrophilic. DMTA results showed an increase in mechanical loss factor (tan δ) for all the reprocessed composites showing a more viscous than elastic nature. The glass transition temperature of fourth cycle composites increased due to polymer dehydrochlorination and the resulting cross-linking, which restricted the molecular mobility of the polymer chains.

According to Augier et al [9], twenty extrusion-milling cycles of internal waste of poly (vinyl chloride) (PVC) and wood fiber-reinforced PVC composite were performed and the mechanical and thermal properties evaluated. This comparison provided evidence of the influence of the vegetable fibres on the thermo-mechanical degradation of the composite material. Up to five cycles, the composite properties remained stable. But after 10 cycles and especially at 20 cycles, the flexural strength increased, whereas the other mechanical properties remained almost constant. At the same time, a decrease of the degradation temperature revealed a deterioration of the molecular structure. The PVC properties remained constant, whereas a great increase in the impact strength was observed after 20 cycles without deterioration of the molecular structure. The different behaviors between the composite and the PVC were explained by the influence of the fibres, which accelerated the PVC degradation, characterized by dehydrochlorination followed by crosslinking reactions.

The study done by Lakhdar et al. [10] was carried out experimentally on three bio-loads of which the chicken feathers are the best of them. The other two bio-loads (cow horns and coconut) decrease elongation at break and also increase rigidity. Adding 10% chicken feathers to the recycled PVC improves flexibility by recovering elongation length at break, and stiffness by reducing stress at break. For these recoverable values, we will be sure to increase the recyclability number of PVC.

This study aims the development of a composite material from the combination of olive husk flour as a filler with PVC as a thermoplastic matrix in the presence of a coupling agent, PVC-g-MA, to improve the interfacial adhesion, which helps to obtain ultimate mechanical and thermal properties.

II.Material and methods

II.1 Material

The used Polyvinyl chloride (PVC), type SE-1200, has K-Wert value of 70.20 to 72.00,viscosity value of 0.99-1.030 and a density of 0.481-0.561

The main additivesof PVC were summarized in table 1.

Table 1: Additives of PVC SE-1200

Additives	Names	Value (%)
Plasticizer	Dioctyl Phthalate (DOP)	30
Stabilizer	Ca/Zn	4
Lubricant	Stearic Acid	0.5

The filler used was olive husk flour; it was obtained after olives processing for oil in the region of Bejaia (Algeria). The olive husk has sustained several pre-treatments, namely washing with hot water to eliminate pulp, drying under ambient conditions for 48 h, grinding, and sieving to have a grain size of ≤100 μm[11].

PVC-g-MA was synthesized at the laboratory of organicmaterials A. Mira University of Bejaia, Algeria by Hammiche et al[12]. The addition of a coupling agent aims for interfacial adhesionimprovement.

II.2 Methods

Preparation of composites

The mixtures are made using a Brabender type mixer, Plasticorder W 50 EHT. The PVC-g-MA compatibilizers and the olive husk flour are first steamed at 60°C for 24 hours. The various

constituents are mixed manually then introduced into the Brabender for 5 min, at a temperature of 180° C. and a rotation speed of 50 rpm.
Mass compositions of the various formulations are given in Table 2.

Table 2: Mass composition of the different formulations

	PVC compound (%)	OHF (%)	PVC-g-MA (%)
PVC	100	0	0
PVC/OHF	80	20	0
PVC/PVC-g-MA/OHF	75	20	5

The processed samples are recycled four times in the internal mixer. These are characterized after each transformation cycle.

Fourier Transform Infrared Spectroscopy (FTIR)

The IR spectra of the virgin PVC and the composites were recorded on a SHIMADZU model FTIR-8400S spectrophotometer, driven by a computer equipped with processing software with a resolution of 4 cm-1, in the region between 4000 cm^{-1} and 400cm^{-1}.

Tensile test

The tensile test allows us to determine the behavior of a material under the effect of a constraint as well as its nature (rigid or flexible). The tensile tests of the PVC/OHF composites were carried out on an MTS synergy RT1000 type tensile machine at ambient temperature (23° C.) and a displacement speed of 2 mm/min. in this study, the results presented are the average of five trials for each sample.

Thermogravimetric analysis (ATG/DTG)

The thermograms of the different samples were recorded using a mettler-type thermogravimetric device, consisting of an ATG/DTG/ATD coupled and plotted by a microcomputer, it is composed of a sample boat of 10 at 30 mg, the boat is introduced into an oven in an inert nitrogen medium with a heating rate of 10° C./min in an interval ranging from 20° C. to 700° C.

III.Results and discussion

Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra of the PVC, PVC/OHF and PVC/PVC-g-MA/OHF formulations at the 1st and 4th transformation cycles are illustrated in figure 1.

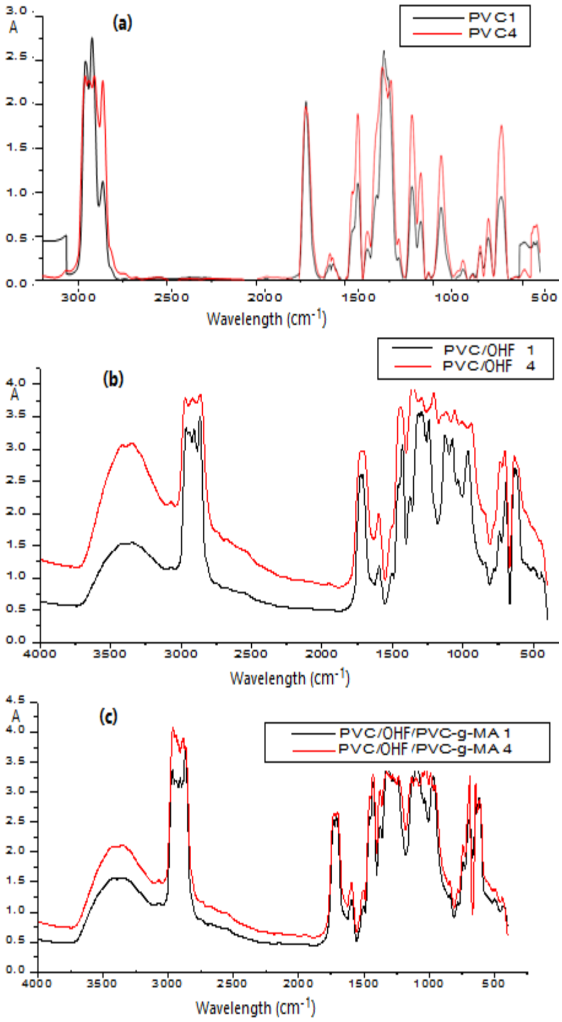

Figure1: FTIR spectra of (a) PVC, (b) PVC/OHF and (c) PVC/PVC-g-MA/OHF formulations at the 1st and 4th transformation cycles.

The FTIR spectra of virgin PVC and composites with and without compatibilizers reveal the presence of an absorption band located at 1735cm^{-1} which can be associated with the carbonyl stretching of the acetyl, aldehyde, carboxyl and ester groups contained in hemicelluloses, lignin and extracts [13]. Moreover, a broad absorption band is observed at 3350 cm^{-1} in composite PVC/OHF samples, which is attributed to the hydroxyl groups contained in the cellulosic of the olive husk flour.
The localized absorption band at about 1600–1630 cm^{-1} is probably associated with absorbed water in crystalline cellulose [14]. After four extrusion cycles no significant change was observed in the infrared spectra of PVC in the carbonyl region

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1700-1850 cm^{-1} which are generated by the oxidative degradation of polyolefin during recycling [15]. We observed a slight increase in carbonyl concentration for composites with and without PVC-g-MA. Similar results are found inthe literature[16-18].

Tensile test

Figure 2 illustrates the evolution of (a) Young's modulus, (b) tensile strength and (c) elongation at break as a function of the number of transformation cycles of PVC, PVC/OHF and PVC/PVC-g-MA/OHF formulations.

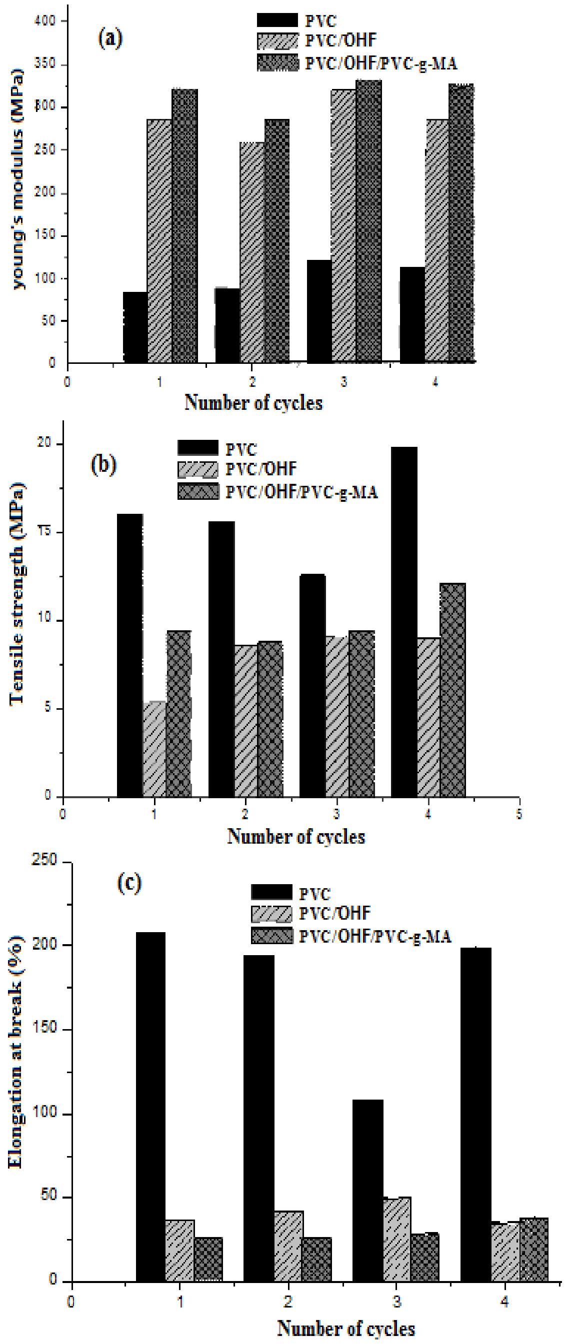

Figure 2: evolution of (a) Young's modulus, (b) tensile strength and (c) elongation at break as a function of the number of transformation cycles of PVC, PVC/OHF and PVC/PVC-g-MA/OHF formulations.

During the first transformation cycle, a significant increase in Young's modulus is recorded with the addition of the charge. However, this increase is more remarkable in the presence of PVC-g-MA.

The Young's modulus of the composites show a strong increase induced not only by the reduction in the dimension of the fibers caused by the grinding but alsoby their good dispersion and therefore an improvement in the interfacial adhesion between the matrix and the reinforcement, especially in the presence of PVC-g-MA and in the third transformation cycle [19,20].

On the other hand, we observed a reduction in the tensile strength of the composites compared to virgin PVC.

The increase in PVC stress is less marked with recycling, there is a slight decrease in stress in the first cycle then an increase in this property in the fourth cycle, and this is probably due to the crosslinking of PVC induced by the setting in implementation [21,22].

However, the increase in the tensile strength of PVC/OHF and PVC/PVC-g-MA/OHF composites is recorded going from 5.4MPa, 9.4MPa respectively in the first cycle to 9MPa, 12.1MPa in the 4th cycle and this is due to a better dispersion of the fiber in the matrix which was due to the reduction of the melt viscosity [23,24].

It is observed that the elongation at break of the PVC matrix isless affected by recycling; it is around 208% in the first processing cycle and 198% in the fourth processing cycle. The addition of the olive husk fiber to the PVC matrix significantly reduces the elongation at break and this is due to the stiffness induced by the vegetable fiber. Generally, the addition of lignocellulosic filler causes a significant decrease in the ductility of the composite [25].

Thermogravimetric analysis (TGA/DTG)

Thermogravimetric analysis makes it possible to follow the variation of the mass of a sample as a function of temperature.

Figure 3 represents the (a) TGA, (b) DTG thermograms obtained from the various virgin PVC, PVC/olive husk and PVC/olive husk/PVC-g-MA formulations during the 1st transformation cycle.

It is noted that the decomposition of PVC occurs in two stages the first stage begins at 270°C and ends around 365°C with a maximum temperature of degradation in the vicinity of 300°C corresponding to a speed of the order of 30% / min and 70% mass loss which is attributed to the dehydrochlorination of PVC and volatile products which consist mainly of HCl, small amounts of benzene, toluene and other hydrocarbons.After this step, the chlorine has been almost completely eliminated. This means that at low temperatures most of the chlorine can be removed from PVC, which forms the basis for other PVC treatment processes. The elimination of HCl molecules lead to the formation of double bonds along the macromolecular chains of PVC, hence obtaining a new polyacetylene polymer [26].

Between 365°C and 415°C, the sample becomes thermally stable, i.e. it does not lose weight at this temperature interval. The second step is linked to the degradation of polyacetylene between 415-520°C to form a residue consisting of carbon black [27]. However, we note that the addition of olive pomace fiber causes a slight decrease in the temperature at which degradation begins, they are of the order of 254°C, 245°C for composites without and with PVC- g-MA respectively, the decrease in decomposition onset temperature for composites treated with PVC-g-MA is due to improved interfacial interaction between the fiber and the matrix by generating strong ester bonds between them [12].

The decomposition of composites takes place in three stages, an exothermic peak located between 250 and 320°C, which corresponds to the thermal depolymerization of hemicelluloses and pectin's, a major secondary decomposition around 390-420°C attributed to the decomposition of cellulose , a last peak representing the decomposition of the residues [28].

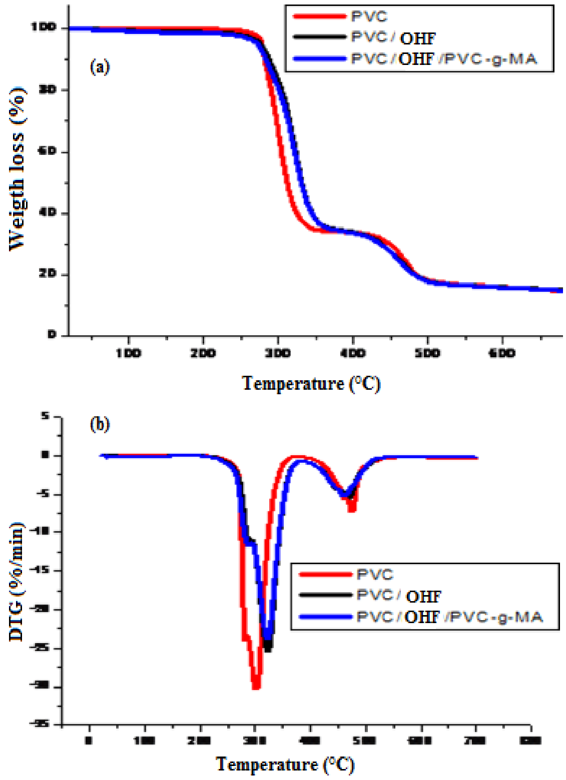

Figure 3: the (a) TGA, (b) DTG thermograms obtained from the various virgin PVC, PVC/olive husk and PVC/olive husk/PVC-g-MA formulations during the 1st transformation cycle.

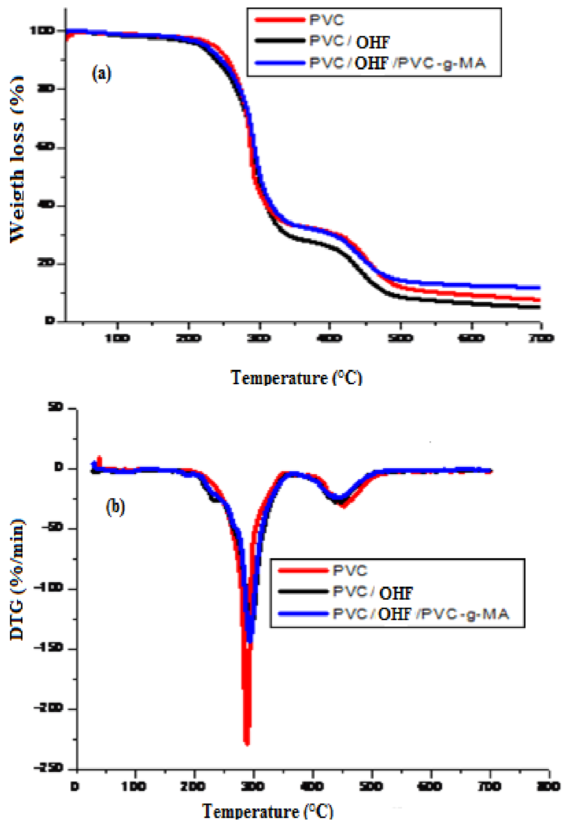

Figure 4: (a) TGA, (b) DTG thermograms of virgin PVC and PVC/OHF, PVC/OHF/PVC-g-MA composites at the fourth recycling cycle.

Figure 4 Represents the (a) ATG, (b) DTG thermograms of virgin PVC and PVC/OHF, PVC/OHF/PVC-g-MA composites at the fourth recycling cycle. We note a decrease in the temperature at which degradation begins compared to composites at the 1st recycling cycle, in fact it is 220°C for virgin PVC and 205°C for composites with and without PVC-g-MA. This decrease is followed by a very rapid decomposition of PVC compared to composites with and without PVC-g-MA. Similarly, we note the decrease in temperature at $T_{50\%}$ of PVC and composites in the fourth cycle and this is due to the increase in molecular weight of PVC and composites.

Contrary to the results of Beg et al [29], weight loss positions on ATG thermograms for PP and composites shifted towards higher temperatures with increasing transformation cycle number, suggesting an increase in thermal stability which is probably due to the increase in crystallinity of PP resulting from the reduction in molecular weight.

The DTG thermograms also show that the maximum rate of degradation of virgin PVC is higher than that of composites, however this parameter decreases according to the number of transformation cycles[30,31].

VI. Conclusions

In conclusion, the aim of this work is to study the mechanical and thermal properties of PVC/olive husk composites with and without PVC-g-MA according to the number of recycling they have undergone.

The results showed that the mechanical properties of the composites increase with the number of extrusion cycles, the tensile strength and the Young's modulus in the studied formulations increased considerably. On the other hand, the infrared spectra show no significant change after four extrusion cycles.

It is also important to take into account the evolution of the thermal properties of the composites after the transformation cycles. We noticed that the addition of olive husk flour causes a slight decrease in the temperature of onset of degradation. So it plays an important protective role; by slowing down its rate and speed of degradation.

Overall this study indicates that PVC/olive husk flour composites represent a good quality for use after multiple recycling especially in the presence of the accounting agent.

Conflict of interest

The authors declare that they have no conflict forfinancial interests or personal relationships that how
can influence the work reported in this paper.

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